REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	11/24/97	Final 6/30/94 - 6/29/97

4. TITLE AND SUBTITLE
Coherent Phonon Modulation of the Electronic Properties of Narrow-Gap Materials

5. FUNDING NUMBERS
F49620-94-1-0308
3484/TS
AFOSR-TR

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8. PERFORMING ORGANIZATION REPORT NUMBER
97-0600

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of Scientific Research/PKA
110 Duncan Avenue, Suite B115
Bolling A.F.B., DC 20332-0001
NE

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

FINAL REPORT 1997

Air Force Office of Scientific Research

AASERT Grant. No. F49620-95-1-0308

Project Period: June 30, 1994 - June 29, 1997

"Coherent Phonon Modulation of the Electronic Properties of Narrow-Gap Materials"

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AASERT Final Report

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Principal Investigator: Erich P. Ippen

Coherent Phonon Modulation of the Electronic Properties of Narrow-Gap Materials

During the three years of this grant, progress was made on several topics related to coherent phonons:

A: Displacive excitation of coherent phonons
B: Optical acoustic phonon coupling in glass fibers
C: Carrier-phonon scattering in semiconductors
D: Coherent optical phonon generation in superconducting C_{60}

The progress in each is reviewed in the Technical Report below. More detailed discussion and experimental details are given in the references to the journal articles and PhD theses that resulted.

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Technical Report

A: Displacive excitation of coherent phonons

Large amplitude coherent optical phonons were observed in series of semimetals and low bandgap semiconductors. We believe that these large amplitudes produce significant modulation of the electronic bandstructure at terahertz frequencies as well as modulation of the dielectric constant. To explain the generation process we developed a theoretical model which we refer to as displacive excitation of coherent phonons (DECP). It confirms the observed symmetry of excitation, the photon energy dependence of the excitation and the initial phase of the coherent oscillation. At low-intensity femtosecond-pulse excitation the frequency and dephasing of the excited phonons are consistent with those of the fully symmetric A_{1g} modes observed in conventional Raman scattering. At higher intensity we observe amplitude-dependent frequency shifts. In the narrow gap semiconductor Ti_2O_3 we observe initial frequency shifts of 7%, in single crystal antimony

as large as 9%. The relaxation of these shifts is directly related to the time-evolving curvatures of the ionic potential in the crystal. We believe that the mechanism for the shifts is a plasma screening of the bare-ion potential. A "dressed" phonon results, with reduced frequency. In our experiments therefore we directly measured the relaxation o the carrier-ion screening process.

1) T. K. Cheng, PhD Thesis, Department of Electrical Engineering and Computer Science, MIT, 1994, "The Excitation and Dynamics of Coherent Lattice Vibrations in Semimetals and Narrow-gap Semiconductors"

2) T. K. Cheng, M. S. Dresselhaus and E. P. Ippen, "Direct Observation of Ultrafast Ionic Screening," Ultrafast Phenomena VI, Springer Series in Chemical Physics, Vol **60**, 301-3, Springer Verlag (1994)

3) H. J. Zeiger, T. K. Cheng, E. P. Ippen, J. Vidal, G. Dresselhaus and M. S. Dresselhaus, "Femtosecond studies of the phase transition in Ti_2O_3," Phys. Rev. B, **54**, 105-123 (1996)

B: Optical acoustic phonon coupling in glass fibers

We demonstrated a new technique for studying the stimulated Raman gain spectrum in glass. We it we were able to measure the low-frequency-shift gain down to shifts as low as 6 cm^{-1}. It is this region of the gain spectrum that is responsible for the Raman self-frequency shift as well as for noise generation in optical squeezing experiments. Two Ti:sapphire laser beams were arranged to propagate in opposite directions through 700 m of single-mode polarization-preserving fiber. The pump beam was narrow-band single frequency, but the probe beam was comprised of femtosecond pulses that had been spectrally broadened to a bandwidth of 60 nm. This short-pulse broadband probing made it possible to obtain the Raman gain spectrum over large Stokes and anti-Stokes detunings simultaneously, with resolution limited only by the spectrometer. Fits of the observed spectrum clearly demonstrate that the gain varies quadratically at low detunings rather than linearly as is conveniently assumed in most analyses of self-frequency shift. Out data also revealed a new oscillatory signal due to Brillouin coupling between pump and probe. The spectral oscillations observed with three different fiber lengths are shown in Figure 1, where they are also compared with predicted curves based on a theoretical model developed after the observations. They are unique to the backward scattering geometry employed in our experiments. When the forward propagating probe pulses are polarized parallel to the pump, the spectral oscillations always occur on the anti-Stokes side of the pump wavelength and move with the center wavelength as the pump is tuned. For cross-polarized probe the oscillations are completely absent.

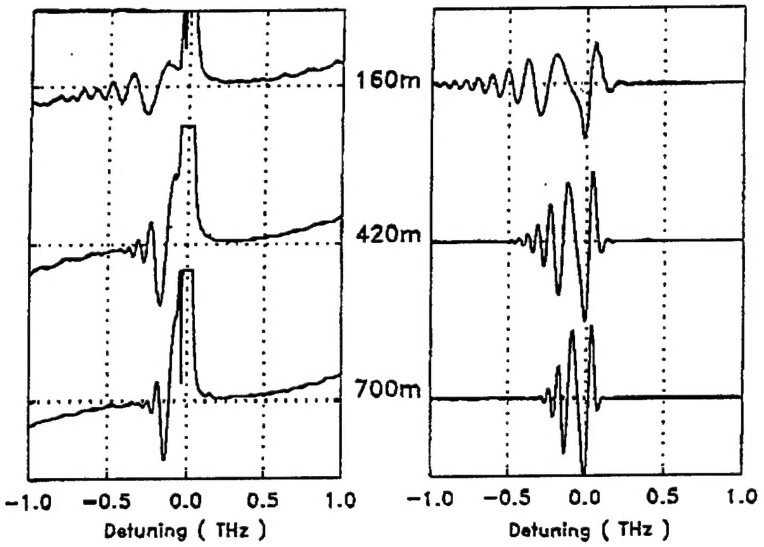

Figure 1: Measured (a) and calculated (b) spectral oscillations for fiber lengths of 160, 420, and 700 nm

An abbreviated description of the phenomena is as follows: The beating of the pump and probe beams drives coherent acoustic modes of the glass through electrostriction. Because of the rapid frequency sweep of this driving force, it acts as an impulse to the low-frequency (20 GHz) modes of the glass. The pump is then resonantly reflected by the resulting traveling acoustic grating. It will also be reflected with the same, bunched, temporal envelope as the acoustic pulse. Finally, since this Brillouin pulse travels with the probe, it coherently cross-phase modulates the probe. Because of the chirp on the probe, this temporal modulation is transferred to the probe spectrum as well.

We do not believe that this effect is limited only to our particular experimental arrangement. In analog fiber communication systems operating near the Brillouin threshold, significant amounts of backscattered light will be present. The noise contributed to transmitted signals as a result of depletion of the carrier by this spontaneous Brillouin scattering has been show to be limited to the Brillouin gain linewidth. Mixing between the carrier and stochastic Brillouin fields by the mechanism described above can impress phase noise on signals at frequencies well beyond that bandwidth.

1) D. J. Dougherty, F. X. Kaertner, H. A. Haus and E. P. Ippen, "Measurement of the Raman gain spectrum of optical fibers," Opt. Lett. **20**, 31-33 (1995)

Carrier-phonon scattering in semiconductors

Femtosecond pump-probe investigations of hot carrier dynamics in semiconductors have been complicated by the variety of effects caused by carrier creation during the pumping process. Thermalization and cooling dynamics of the injected electron and hole distributions can be masked by screening of the Coulomb attraction between electron-hole pairs and by bandgap renormalization. This is particularly true in II-VI semiconductors like ZnSe where we have observed the bandedge nonlinear response to be dominated by the screening. To study the hot carrier dynamics we have introduced a different approach: we use doped materials in which the Coulomb attraction is already screened, and we use below-band pump pulses which heat the free carriers but create no new carriers. This approach is made possible by a wavelength-tunable femtosecond Ti:sapphire laser which provides the infrared pump pulses directly and which can be frequency-doubled to provide 60 fs probe pulses tunable near the ZnSe bandedge. The relationship between the excitation and probing photon energies and the ZnSe bandgap and conduction band structure is shown in Figure 2.

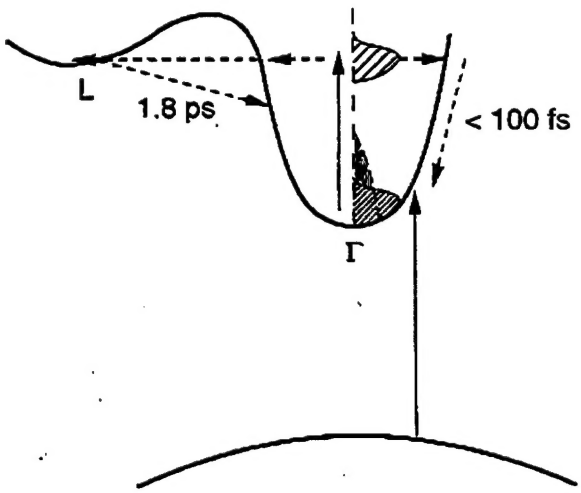

Figure 2: Schematic of the pump-probe experiments in ZnSe. Free carriers in the conduction band are heated by a below band pulse. Heating and cooling of the bandedge distribution is then probed by the shorter wavelength probe.

Following the infrared excitation the carrier distribution is rapidly heated, in less than 100 fs. The probe can be tuned through this distribution to reveal the nature of the Fermi smearing and to monitor the cooling via carrier-phonon coupling. The carrier cooling dynamics due to carrier-phonon coupling are thereby isolated from carrier creation dynamics. In our experiments we determined relaxation times of 500 fs for electrons and 900 fs for holes, in N- and P-type samples respectively. These times are considerably longer than the times predicted by present theory, a fact that calls for revisiting the theory.

In these studies, a delayed carrier heating response was also evident in the N-type samples, as shown in the data of Figure 3 below.

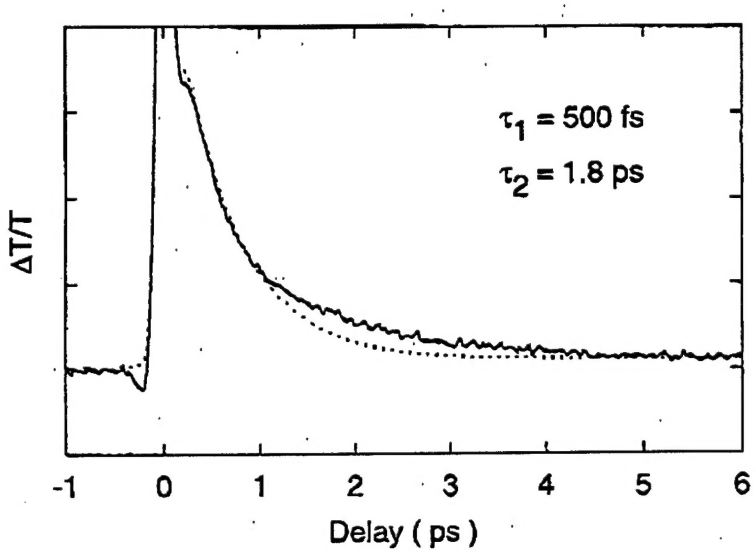

Figure 3: The time-resolved transmission change for the N-doped samples shows a 500 fs decay rate due to electron-phonon coupling at all excitation wavelengths. In a range above a threshold photon energy, an additional 1.8 ps component was also apparent. Only the relative magnitudes of these components changed, not the time constants.

As the infrared pump pulses were tuned, the magnitude of this response varied; and a photon energy threshold was identified. The threshold nature indicates the opening of a new scattering pathway; optical phonon scattering to an L-valley minimum 1.31 eV above the Γ-valley. This energy offset was not known previously with such accuracy. The relative magnitude of the delayed heating response observed in this way is a measure of the efficiency of the phonon-assisted scattering to the L-valley: we measure a partition as great as 50% near the valley minimum. The time constant of the delayed heating response determines the L-Γ scattering time that governs the return of the carriers: for that we measure a time of 1.8 ps. This was we believe the first direct measurement of such an intervalley scattering time.

1) D. J. Dougherty, S. B. Fleischer, E. L. Warlick, J. L. House, G. S. Petrich, E. Ho, L. A. Kolodziejski and E. P. Ippen, "Ultrafast carrier dynamics and intervalley scattering in ZnSe," to be published in Appl. Phys. Lett.
2) D. J. Dougherty, PhD Thesis, Department of Physics, MIT, 1997, "Femtosecond optical nonlinearities in ZnSe and characterization of ZnSe/GaAs heterostructures."

Coherent phonons in doped C_{60}

Ultra-sensitive pump probe studies were also performed on thin films of the doped fullerenes K_3C_{60} and Rb_3C_{60}. Both were determined to be superconducting (at 18K and 28K respectively). When pulses as short as 20 fs were used, the impulsive excitation of coherent phonon oscillations was observed. The excited oscillations corresponded to the A_g1 mode at a frequency of about 495 cm^{-1}, approximately the same as that observed in incoherent Raman scattering experiments. A remarkable number of oscillation periods ((200 periods of the A_g1 mode) are observed, to our knowledge the largest number of phonon oscillations reported in a time-resolved measurement on any system. Critical to this observation is our recent development of shot-noise-limited pump-probe sensitivity. In this case, even with the low average powers required (a few tens of microwatts) a minute signal modulation of only 10^{-7} could be detected on the probe beam. Figure 4 shows a typical time-resolved reflectivity signal showing this modulation. Figure 5 shows an expanded version of the coherent phonon signal, after the slower background decay has been removed. Also indicated on Figure 5 are the amplitude and initial phase of the A_{g1} oscillations deduced from a theoretical fit.

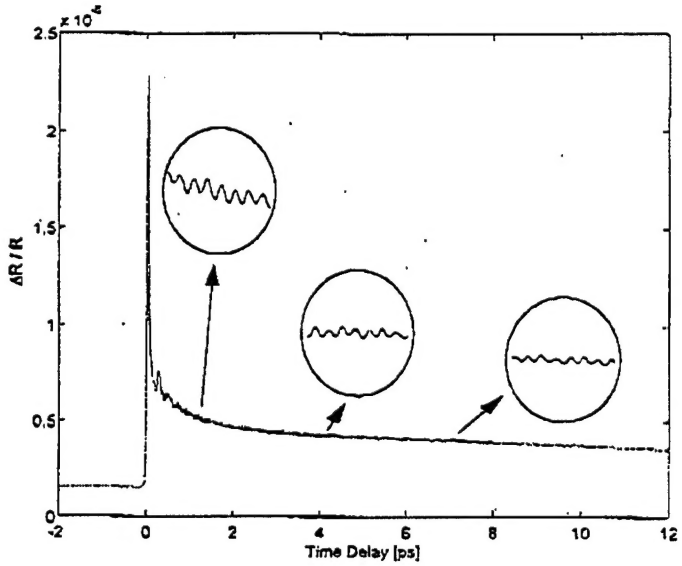

Figure 4: The coherent phonon oscillation in K_3C_{60} at 300K. The pump-probe data were taken with a time resolution of about 20 fs. The circular insets magnify the minute oscillations.

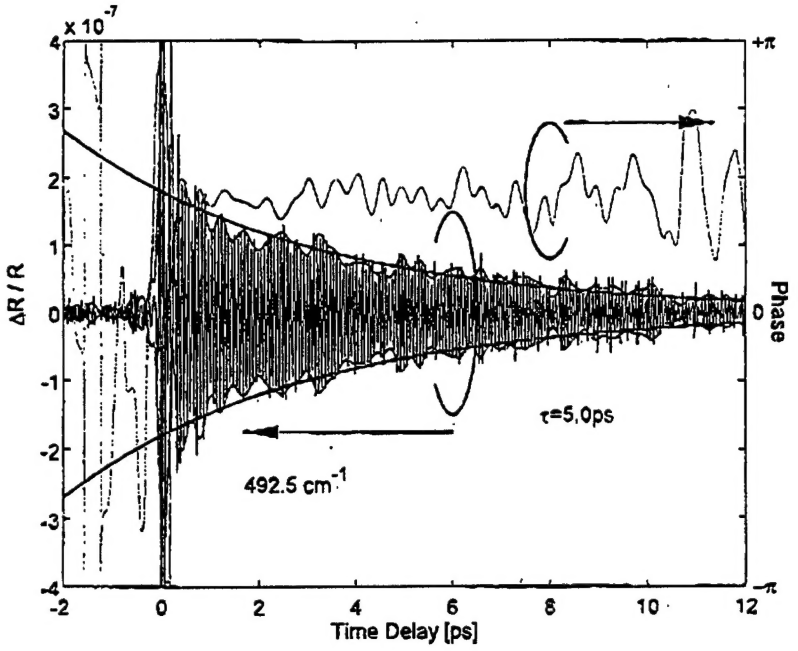

Figure 5: The oscillatory behavior in the pump-probe data for K_3C_{60} obtained after subtracting the instantaneous and smoothly decaying components. The amplitude response indicates a 5 ps dephasing time for the coherent phonons.

A slight dependence of the coherent phonon frequency on dopant could be detected (a 2.5 cm^{-1} difference of the coherent phonon frequency between K_3C_{60} and Rb_3C_{60}). Our measurements also revealed, for the first time, a vibrational mode at about 150 cm^{-1} which we attribute to a beating between the C_{60} anion and the alkali-metal cation. The dephasing time for this oscillation is very fast (1-2 periods) which explains, we think, why it has not been possible to observe it by spontaneous Raman spectroscopy. Such a highly damped mode has a low peak scattering cross-section and a very broad linewidth. In such cases, as demonstrated by our results, time-resolved techniques such as pump-probe are not only superior to conventional methods they can reveal new behavior.

1) S. B. Fleischer, B. Pevzner, D. J. Dougherty, E. P. Ippen and M. S. Dresselhaus, "Phototransformation in visible and near-IR femtosecond pump-probe studies of C60 films," Appl. Phys. Lett. **69**, 296-8 (1996)
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